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A SMOKING ARTICLE INCLUDING A SELECTIVE CARBON MONOXIDE PUMP

Background of the Invention

5 The present invention relates generally to smoking article and, more particularly, to a carbon monoxide pump for removing carbon monoxide from main stream smoke during the combustion of a smoking article.

Investigators have been trying now for about twenty years to find ways to lower the amount of carbon monoxide experienced by smokers when main stream smoke is inhaled. One of the issues with respect to carbon monoxide is the amount of carbon monoxide actually contained or produced by a smoking article. For example, an average amount of carbon monoxide produced by a smoking cigarette is as high as about 10-15 milligrams (mg). To adsorb this amount of carbon monoxide would require a very large amount of adsorbent for carbon monoxide if it was all intended to be trapped by such an adsorbent. This is impractical and cost prohibited.

An alternative approach to adsorbing carbon monoxide is to oxidize it, for example, by the catalytic oxidation to carbon dioxide. A difficulty with this approach is that the temperature of the main stream smoke is substantially that of the environment. These low temperatures make it difficult to oxidize carbon monoxide to carbon dioxide even when using a catalyst.

Thus, there remains a need for a method and apparatus for carbon monoxide reduction in cigarette smoke.

Summary of the Invention

25 The present invention fulfills this need by providing a smoking article including a tobacco column; a wrapper surrounding the tobacco column; and a carbon monoxide pump. The pump includes an adsorbent for adsorbing carbon monoxide and may include a catalyst for oxidizing carbon monoxide to carbon dioxide. In use, the carbon monoxide pump selectively diverts carbon monoxide from main stream combustion products, the catalyst at least partially oxidizes the carbon monoxide to carbon dioxide and the venting holes provide an alternative path for the diverted carbon monoxide and the oxidized carbon monoxide to reduce inhalation by a

smoker. In a preferred embodiment, venting holes adjacent to the adsorbent facilitate the further diversion of carbon monoxide from main stream smoke

A preferred catalyst is a transition metal including rare earth metals and a platinum group metal. Preferred transition metals include at least one of copper, cobalt, iron, silver, nickel, their alloys, their mixtures and combinations thereof, with silver being the most preferred. The transition metal may be elemental, an oxide, or combinations thereof.

In an embodiment, the CO pump includes at least one additional filter element, preferably cellulose acetate. A catalyst may be distributed through the at least one additional filter element

In the vicinity of the adsorbent, the concentration of carbon monoxide is increased, thereby increasing the flux of carbon monoxide from the adsorbent. The adsorbing is momentary, preferably for between about 0.1 and about 10 seconds.

In a preferred embodiment, the adsorbent is a zeolite such as an oxide, more preferably, at least one of silicon, aluminum, magnesium, their mixtures and their compounds. A dehydrated oxide, particularly of aluminum has been found to be effective. An amorphous oxide may also work. In a preferred embodiment, the adsorbent is a support for the catalyst.

Accordingly, one aspect of the present invention is to provide a smoking article including a tobacco column; a wrapper surrounding the tobacco column; and a carbon monoxide pump including an adsorbent for adsorbing carbon monoxide, wherein the carbon monoxide pump is aligned with the tobacco column so as to selectively divert carbon monoxide from main stream combustion products prior to inhaling by a smoker.

Another aspect of the present invention is to provide a carbon monoxide pump for use in a smoking article including a tobacco column and a wrapper surrounding the tobacco column. The carbon monoxide pump includes an adsorbent for adsorbing carbon monoxide, and a catalyst. When placed adjacent to the tobacco column, the carbon monoxide pump selectively diverts carbon monoxide from main stream combustion products by adsorbing carbon monoxide, and the catalyst at least partially oxidizes the diverted carbon monoxide to carbon dioxide prior to being inhaled by a smoker.

Still another aspect of the present invention is to provide a smoking article including a tobacco column; a wrapper surrounding the tobacco column; and a carbon monoxide pump. The pump includes an adsorbent for adsorbing carbon monoxide; a catalyst for oxidizing carbon monoxide to carbon dioxide, and venting holes adjacent to the adsorbent. In use, the carbon monoxide pump selectively diverts carbon monoxide from main stream combustion products, the catalyst at least partially oxidizes the carbon monoxide to carbon dioxide, and the venting holes provide an alternative path for the diverted carbon monoxide and the oxidized carbon monoxide to reduce inhalation by a smoker.

10 The invention also provides a mouthpiece for a smoking article including a fitting to receive a smoking article, and a carbon monoxide pump including an adsorbent for adsorbing carbon monoxide, wherein the carbon monoxide pump is positioned with respect to the smoking article so as to selectively divert carbon monoxide from main stream combustion products prior to inhaling by a smoker.

15 These and other aspects of the present invention will become apparent to those skilled in the art after a reading of the following description of the preferred embodiment when considered with the drawings.

Brief Description of the Drawings

20 FIGURE 1A is a smoking article according to the present invention;
FIGURE 1B is an exploded view of the smoking article of Figure 1A;
FIGURE 2 is a schematic of a tobacco column adjacent to a selective carbon monoxide pump according to the present invention;
FIGURE 3 is a block flow diagram for a carbon monoxide pump according to
25 the present invention; and
FIGURE 4 is a partial perspective view of a mouthpiece according to the invention.

Description of the Preferred Embodiments

30 Referring now to the drawings in general and Figure 1 in particular, it will be understood that the illustrations are for the purpose of describing a preferred embodiment of the invention and are not intended to limit the invention thereto. As

best seen in Figures 1A and 1B a smoking article includes a wrapper 12 surrounding a tobacco column 14 adjacent to carbon monoxide pump 16. Preferably, the pump 16 selects carbon monoxide for diversion from main stream smoke. A further feature of the embodiment shown in Figure 1 is the presence of venting holes 18. As best seen in Figure 1B, which is an exploded view of the smoking article in Figure 1A, the wrapper 12 surrounds tobacco column 14. As best seen in Figures 1B and 2, the selective carbon monoxide pump 16 may be placed adjacent to, but not necessary abutting the tobacco column 14. Typically it is aligned with the tobacco rod so that smoke from the tobacco combustion passes through the pump 16. Other paths that expose the smoke to the pump may be used.

Additionally, as seen in Figure 2, at least one additional filter element 24 may be included in the smoking article 10. Although Figure 2 depicts the selective carbon monoxide pump 16 between two additional filter elements 24, there may be a single additional filter element 24. In such case, the at least one filter element 24 may be at either between the tobacco column 14 and the selected carbon monoxide pump 16. Alternatively, the carbon monoxide pump 16 may be between the tobacco column 14 and the at least one additional filter element 24. The filter element 24 is typically of a conventional filter material such as cellulose acetate.

In operation, the selected carbon monoxide pump 16 diverts carbon monoxide from main stream smoke to, for example, side stream smoke. A block diagram of the pump's operation is seen in Figure 3. Starting at the top of Figure 3, after a smoking article 10 including the carbon monoxide pump 16 is lit, a smoker draws on the article from the filtered end. As the smoker draws on the smoking article 10, the combustion products are drawn through the carbon monoxide pump 16 for diverting carbon monoxide from the main stream smoke.

In an embodiment having a catalyst, the carbon monoxide diverted from the combustion products interacts with the catalyst and is oxidized to carbon dioxide. When venting holes 18 are placed proximate to the carbon monoxide pump, the carbon dioxide is expressed through the venting holes 18 and inherent pores in the wrapping paper around the carbon monoxide pump 16. The inclusion of venting holes 18 proximate to the carbon monoxide pump 16 and the inherent porosity provide a passage for the oxidized carbon monoxide, which is carbon dioxide, to be

expressed from smoking article. In embodiments having no venting holes 18, inherent pores within the paper provide a path for the expression of oxidized carbon monoxide. Carbon dioxide, generated from carbon monoxide, may also remain in the main stream smoke, providing no harm to the smoker.

5 In an alternative embodiment, having no catalyst, the carbon monoxide pump 16 includes an adsorbent material. In this embodiment, as the main stream smoke passes over the adsorbent material, carbon monoxide is adsorbed from the main stream smoke onto the adsorbent material. During the delay between the current puff and the successive puff, which may be called an inter-puff period, the concentration
10 of carbon monoxide increases in gas phase within the adsorbent material due to its desorption. The higher concentration of the carbon monoxide in the vicinity of the adsorbent material creates a driving force that increases the flux of carbon monoxide from the adsorbent material so that it exits holes 18 proximate to the carbon monoxide pump 16.

15 As best seen in Figure 3, the drawing, diversion and expression cycles continue during the consumption of the smoking article and in this manner, the amount of carbon monoxide inhaled by the smoker is substantially reduced.

The following examples provided to give a better understanding of the invention and its operation through a discussion of the synthesis, testing and
20 characterization. The examples are in no way meant to limit the scope of the claimed invention.

Example 1. Gas chromatographic analysis using a Model No. 6890, manufactured by Hewlett Packard, and an infrared CO sensor, manufactured by Filtrona, Inc., were used to determine the gas phase content of cigarette smoke under
25 standard smoking conditions using a filling machine, manufactured by Filamatic, Inc., reconstructed to a smoking machine. As part of this analysis, the removal of CO from the gas was studied using an artificial mixture comprising helium with about 2% carbon monoxide by volume. About 1% by volume nitrogen was added to this mixture as an internal standard. Catalytic oxidation of CO was also studied using a
30 mixture of helium, about 2% CO by volume, and about 13% oxygen. The above concentrations were prepared to simulate the average characteristics of tobacco smoke.

zeolite possessed substantially the same CO adsorption activity as that of an about 5Å dehydrated sample. Results also suggest that zeolites with a pore size of about 5Å or greater may be used as a starting material to develop a carbon monoxide pump that diverts CO from main stream smoke.

5 Example 3. An Ag₂O/ about 5Å zeolite and an Ag₂O/about 9Å 13X zeolite catalyst/adsorbents were prepared. About 5 grams (g) of silver nitrate were dissolved in about 15 ml of an about 10M NH₄OH solution that was then combined with water for dilution to about 50 ml. About 20g of about 0.4 to about 0.8 millimeter (mm) beads of a zeolite were added and allowed to remain
10 overnight for a silver exchange. Each zeolite mixture was shaken frequently for about the first hour to remove evolved air. The catalyst was thoroughly washed with about 2L of water, dried for about 2 hours in air at about 60°C and overnight at about 150°C to decompose [Ag(NH₃)₂]NO₃. After this treatment the resulting light-yellow catalyst was stored in a jar.

15 The removal of CO from a gas was studied using freshly prepared samples in the reactor and the gas mixtures described in Example 1. About 300 milligrams (mg) of each CO pump material were loaded in a filter. Experimental results showed reductions of CO in main stream smoke as high as about 50-60% by volume.

20 Example 4. Catalyst/adsorbent samples comprising Ag₂O-on-about 13X zeolite (about 9Å) from Lancaster, and CP861E (about 7Å) and CBV5524G (about 5Å) from Zeolyst International were prepared substantially as described in Example 3. Atomic absorption analyses using a Spectr AA-100, manufactured by Varian, provided the concentrations of silver in the samples. These
25 concentrations are summarized in Table 1 and the corresponding CO removal activities are summarized in Table 2.

Table 1: Concentration of Silver in Zeolite-Supported Catalysts/Adsorbents from AA Analysis Data.		
Sample	Support	% silver
1	13X zeolite (Lancaster)	8.5
2	CBV5524G (NN 2..4 are from Zeolyst)	4.0
3	CP861E (exchanged/milled/sieved)	10.0
4	CP861E (milled/sieved/exchanged)	7.8

Also, zeolites containing silver showed high activity in the catalytic oxidation of CO at higher temperatures. A study of the kinetics of oxidation of CO on silver oxide and a partially reduced silver catalyst revealed that silver catalysts reduced at about 110-150°C were more active in oxidation of CO, and
 5 may provide about 70% removal of CO from main stream smoke. However, applicants believe that an excessively active catalyst may provide poor CO removal because of its irreversible deactivation by of other combustion products (see for example sample 2 in Table 2 having a small zeolite pore size).

Table 2: CO Removal from Main stream Smoke by Modified Cigarette Filters, Containing Ag/zeolite CBV5524G (about 5Å)

Sample	Filter and Cigarette	% CO removed
1	Ag ₂ O/Z in vented filter	about 60
2	#1, reduced CO at about 120°C	about 0
3	Ag ₂ O/Z in non-vented filter	about 22
4	Ag ₂ O/Z in tobacco	about 37

10 Note: Sample 4 contained approximately the same amount of Ag/zeolite adsorbent, but distributed in the tobacco.

The results summarized in Table 3 indicate that a similar treatment of Ag/zeolite at about 120°C in a reducing gas containing CO may led to an increase
 15 in CO removal from about 50 to about 71%, when zeolite as large as about 9Å was used. Even after about 3 hours in humid room air, CO removal activity was not decrease and was measured as at about 81%. These results were confirmed when zeolite CP861E with an aperture size of about 7Å was used. Corresponding data are summarized in Table 5.

20 As indicated by the results summarized in Table 3, a higher reduction temperature of about 150°C does not further improve the performance of a catalyst compared to the sample, heat-treated at 120°C. These results imply that a partial reduction of silver in a Ag/zeolite adsorbent/catalyst may be a useful treatment, positively affecting the CO removal effectiveness. CO removal
 25 conditions however, must be carefully predetermined and controlled to avoid an over-reduction of silver.

As the results summarized in Table 2 shows, an about 5Å zeolite, used in a non-vented cigarette, provides a lower degree of CO removal of about 22%.

Table 5. CO Removal from Main stream Smoke by
Modified Vented Cigarette Filters
Containing Ag/zeolite CP861E (about 7Å).

Sample	Filter	%CO removed
13	Ag ₂ O/Z	about 42
14	#13, reduced CO at 120°C	about 56
15	#14, oxidized 5 hrs in air at room T	about 37

Note: Zeolite was modified, milled and sieved to about 40-60 mesh.

Table 6. CO Removal from Main stream Smoke by
Modified Cigarette Filters
Containing Ag/zeolite CP861.

Sample	Filter and Cigarette	%CO removed
16	Ag ₂ O/Z in vented filter	about 73
17	#16, kept in cigarette for 2 hrs	about 48
18	#16, kept in cigarette for 1 day	about 45
19	#16, kept in cigarette for 2 days	about 26
20	#16, kept in cigarette for 3 days	about 22
21	#16, kept in cigarette for 10 days	about 50
22	Ag ₂ O/Z in non-vented filter	about 27
23	#22, kept in cigarette for 0.5 hr	about 9

Note: Zeolite was milled, sieved 40-60 mesh and modified with Ag compound.

- 5 A feature of adsorbent preparation appears evident from data summarized in Tables 5 and 6. Sample 13 in Table 5 was prepared beginning with a silver water phase exchange procedure done to whole zeolite grains of about 2x6 mm size. After silver deposition the adsorbent was milled, sieved and packed in a filter. The effectiveness of this filter was about 42%; this effectiveness varied slightly from both an about 120°C reduction material and a long-term storage material.

- 10 Sample 16 in Table 6, was made starting with a milled and sieved CP861 zeolite. Removal of CO by this material exceeded about 70%; its activity remained significant, although reduced, even after about 10 days at about room temperature in a vented CO pump. This result suggests that it may be preferred to a shape and sieve a zeolite prior to silver incorporation.

Example 5. Nickel oxide particles, modified with the rare-earth element dysprosium, were embedded into large-pore molecular sieves. These materials readily adsorb substantially all of the GC-detected, gas-phase organic molecules

except light hydrocarbons. The filtering properties of the adsorbent appeared to be similar to that of activated carbon. The Ni/Dy/zeolite system also demonstrated significant carbon monoxide adsorption activity.

About 10g of nickel acetate $\text{Ni}(\text{CH}_3\text{HOO})_2 \cdot 4\text{H}_2\text{O}$, from the Fisher Company, dissolved in 100 ml water, were mixed with about 30g zeolite CBV300-X16 from the Zeolist International Company. The zeolites were used as about 1x4 mm extruded granules. The mixture was retained at about room temperature for about 5 days to facilitate nickel ion exchange. The solution was then decanted and the zeolites were thoroughly washed with cold water.

About 3g of dysprosium chloride DyCl_3 (grade REO), from Strem Chemicals, were dissolved in about 50 ml water and mixed with the solid material. The mixture was retained at about room temperature for about 5 additional days to exchange Dy^{3+} ions into the matrix. The solution was decanted. The solid material was washed with plenty of water, dried at about 50°C for about 2 days and annealed at about 350°C for about 2 days in air. The catalyst was stored in air as about 1x4 mm granules. Before conducting experiments, the sample was milled and about 40-60 mesh size particles were sieved off to be used in a CO pump.

About 500 mg of the catalyst were packed adjacent to tobacco in non-vented and vented research cigarettes. About 70% CO removal from main stream smoke was obtained in both cases. Also, GC analysis of the filtered tobacco smoke showed about 90% removal of acetaldehyde, acrolein and other functional derivatives, as well as unsaturated hydrocarbons. The adsorbent behaved essentially like an activated carbon with respect to these compounds (e.g., low selectivity).

Example 6. Zeolite samples impregnated with copper and palladium ions were similarly prepared using their corresponding chlorides. Palladium salt was dissolved in aqueous HCl so that the H_2PdCl_4 complex was used in place of the ammoniacal complex.

Copper- and palladium-containing zeolite of about 5Å showed minor CO activity at about room temperature. Applicants believe that the high temperature activity and sensitivity to poisons (both known characteristics of copper and

palladium compounds) explain the results.

Example 7. Three samples were formed by distributing hydrochloric acid-doped polyaniline in both about 3Å and about 9Å zeolite samples, and on the surface of a cellulose/acetyl cellulosic cigarette filter. About 5g of the
5 corresponding zeolite or the cellulose acetate filters, taken from research cigarettes, were placed in about 300 ml solution of 5g aniline in an about 1M aqueous HCl. This suspension was mixed for about 20 hrs at about room temperature for aniline adsorption on carbon. The resulting solids were filtered and washed with about 500 ml water and about 100 ml of an about 1M HCl
10 solution. The supported aniline was suspended in about 300 ml of an about 1M HCl solution that was then cooled on ice.

About 11g of ammonium persulfate (about 98% pure) were dissolved in about 200 ml of an about 1M HCl solution. The solution was cooled on ice and slowly added to the suspension, while maintaining the temperature below about
15 10°C under a vigorous magnetic stirring. The temperature was allowed to self-equilibrate to about room temperature in about 2 hrs and stirring was continued for about another 20 hrs.

The resulting solids were filtered and washed with about 1L water on a filter and suspended in about 300 ml of an about 1M NH₄OH solution under
20 mixing for about another 20 hrs. The supported polymers were washed with about 1L of water on a filter. The solid materials were suspended in about 300 ml of an about 1M HCl solution under mixing for about another 20 hrs. The final products, the HCl-doped supported polymers, were thoroughly washed in about 2L of water, filtered, dried in air at about room temperature for about 24 hrs and
25 stored.

Polyaniline embedded into about 3Å and about 9Å zeolite matrices showed very low CO adsorption activity. However, the same polymer supported on a cellulose/cellulose acetate cigarette filter adsorbed CO from the first cigarette puff. The following puffs remained unchanged because of the low
30 adsorptive, irreversible capacity of polyaniline.

The invention can also be carried out by providing a mouthpiece for a smoking article (such as a cigarette or cigar) to which the smoking article is attached

when smoked. If the pumping capacity of the mouthpiece is great enough, it may be reused with multiple smoking articles. The mouthpiece can be configured in numerous shapes and sizes as desired, but an example is seen in Figure 4. The mouthpiece M includes a fitting 22 to receive a smoking article C, and a carbon
5 monoxide pump 24 including an adsorbent 116 for adsorbing carbon monoxide, wherein the carbon monoxide pump is positioned with respect to the smoking article C so as to selectively divert carbon monoxide from main stream combustion products prior to inhaling by a smoker. Vents 20, 118 can be provided like the vents 18 mentioned above. If desired, portions of the mouthpiece M may include a
10 conventional filter material 120, such as cellulose acetate or other filter material.

Certain modifications and improvements will occur to those skilled in the art upon a reading of the foregoing description. By way of example, CO removal may be attempted by changing the smolder of a tobacco column, which in turn changes the chemical makeup of the main stream smoke. Even with changing the smolder of the
15 tobacco column, the present invention may be effective. It should be understood that all such modifications and improvements have been deleted herein for the sake of conciseness and readability but are properly within the scope of the following claims.